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Terminology

- ▶ Natural Attenuation
- ▶ Monitored Natural Attenuation
- ▶ Intrinsic Remediation
- ▶ Intrinsic Bioremediation
- ▶ Passive Bioremediation

Terminology - Con't

- ▶ Natural Assimilation
- ▶ “Wink and Walk” Approach
- ▶ No Action Alternative
- ▶ Bioprocrastination

EPA Definition - Monitored Natural Attenuation

The term Monitored Natural Attenuation Refers to the Reliance on Natural Attenuation Processes (Within the Context of a Carefully Controlled and Monitored Site Cleanup Approach) to Achieve Site-Specific Remedial Objectives Within a Time Frame That is Reasonable Compared to Other Methods

EPA Definition - Natural Attenuation Processes

A Variety of Physical, Chemical, or Biological Processes that, Under Favorable Conditions, Act Without Human Intervention to Reduce the Mass, Toxicity, Mobility, Volume, or Concentration of Contaminants in Soil or Groundwater.

These In-Situ Processes Include Biodegradation, Dispersion, Dilution, Sorption, Volatilization, and Chemical or Biological Stabilization, Transformation, or Destruction of Contaminants

Definitions

- ▶ Natural Attenuation
 - ▶ Dispersion, Dilution, Sorption, Volatilization, Abiotic Degradation, and Biodegradation
- ▶ Intrinsic Bioremediation
 - ▶ Natural Biodegradation

Benefits of Natural Attenuation

- ▶ Complete Mineralization of Contaminants to Innocuous Products
- ▶ Not Just Transferring Compounds to Another Phase or Location
- ▶ Passive Technique - Allows Continuing Use of Infrastructure
- ▶ Cost Effective - More Funds for Problematic Sites

Benefits of Monitored Natural Attenuation - EPA

- ▶ Less Generation or Transfer of Remediation Wastes
- ▶ Less Intrusive as Fewer Surface Structures are Required
- ▶ May be Applied to all or Part of a Given Site, Depending on Site Conditions and Cleanup Objectives

Benefits of Monitored Natural Attenuation - EPA - Con't

- ▶ Natural Attenuation may be Used in Conjunction with, or as a Follow-Up to, Other (Active) Remedial Measures
- ▶ Overall Costs will Likely be Lower than with Active Remediation (With the Possible Exception of Small Fuel Spills)

Potential Drawbacks of Natural Attenuation

- ▶ Subject to Natural and Anthropogenic Changes in Local Hydrogeologic Conditions
 - ▶ Groundwater Gradients/Velocity
 - ▶ Changes in Electron Acceptor/Donor Concentrations
- ▶ Aquifer Heterogeneity May Complicate Site Characterization
- ▶ Time Frame for Completion May Be Prohibitively Long

Potential Drawbacks of Monitored Natural Attenuation - EPA

- ▶ Longer Time Frames may be Required to Achieve Remediation Objectives, Compared to Active Remediation
- ▶ Site Characterization may be More Complex and Costly
- ▶ Toxicity of Transformed Products may Exceed that of the Parent Compound

Potential Drawbacks of Monitored Natural Attenuation - EPA - Con't

- ▶ Responsibility must be Assumed for Long-Term Monitoring and its Associated Cost, and Implementation of Institutional Controls
- ▶ Potential Exists for Continued Contaminant Migration

Potential Drawbacks of Monitored Natural Attenuation - EPA - Con't

- ▶ The Hydrogeologic and Geochemical Conditions Amenable to Natural Attenuation are Likely to Change over Time and Could Result in Renewed Mobility of Previously Stabilized Contaminants and May Adversely Impact Remedial Effectiveness
- ▶ More Extensive Outreach Efforts May be Required in Order to Gain Public Acceptance of Natural Attenuation

Natural Attenuation

- ▶ Determination is Site Specific
- ▶ Site Characterization Must Be Geared Toward Supporting This Remedial Option
- ▶ Burden of Proof is On the Proponent, Not The Regulator
- ▶ Can be Scientifically Supported

Mechanisms of Natural Attenuation

- ▶ Non-Destructive Attenuation Mechanisms
 - ▶ Sorption, Dispersion, Dilution from Recharge, and Volatilization
- ▶ Destructive Attenuation Mechanisms
 - ▶ Biodegradation
 - ▶ Aerobic
 - ▶ Anaerobic
 - ▶ Abiotic Oxidation Processes
 - ▶ Hydrolysis

Non-Destructive Attenuation Mechanisms

Results in Decreasing Contaminant Concentration
but Not Removal of Contaminant Mass

- ▶ Sorption
- ▶ Dispersion
- ▶ Dilution from Recharge
- ▶ Volatilization

Destructive Attenuation Mechanisms

Results in Destruction of Contaminant Mass

- ▶ Biotic
 - ▶ Electron Donor Reactions
 - ▶ Electron Acceptor Reactions
 - ▶ Cometabolism
- ▶ Abiotic
 - ▶ Hydrolysis
 - ▶ Dehydrohalogenation

Major Processes Affecting Dissolved BTEX Fate and Transport

- ▶ Advection
- ▶ Dispersion
- ▶ Sorption
- ▶ Biodegradation

History of Natural Attenuation as a Science - Continued

1990's Continued

California State Water Resources Control Board,
1995, LUFT Historical Case Analysis: Lawrence
Livermore Laboratories.

Evaluated Historical Data From over 1,000 Fuel Spills

33% of Plumes Shrinking

59% of Plumes Stable

8% of Plumes Growing

Most plumes <250 feet Long

History of Natural Attenuation as a Science - Continued

1990's Continued

Kuehne, D., and Buscheck, T.E., 1995,
Evaluation of 119 Gasoline Station Fuel
Hydrocarbon Spills: Unpublished Data.

Evaluated Historical Data From Fuel Spills
at 119 Gasoline Stations

52% of Plumes Shrinking

35% of Plumes Stable

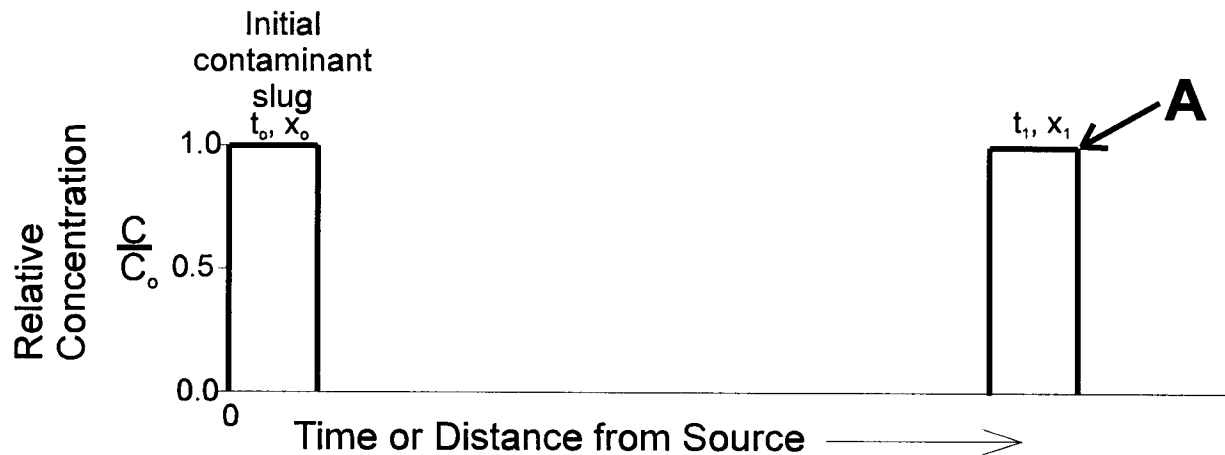
13% of Plumes Undecided (Lack of Data)

92% of Plumes <200 feet Long

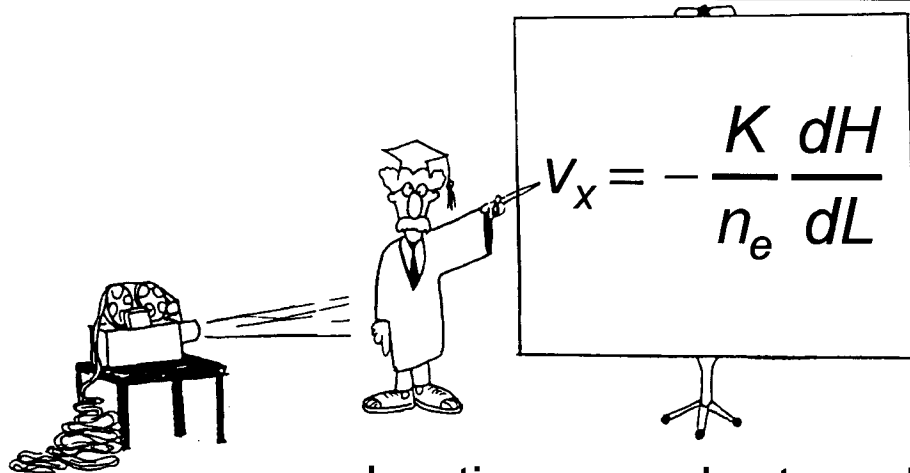
Advection

- ▶ Transport of Solutes by Bulk
Movement of Groundwater
- ▶ Solute Acts Like a Water Molecule
- ▶ Solute Moves at Average Advective
Velocity of Groundwater

Instantaneous Source with Advection Only



Advective (Linear) Groundwater Flow Velocity



v_x = advective groundwater velocity [L/T]

K = hydraulic conductivity [L/T]

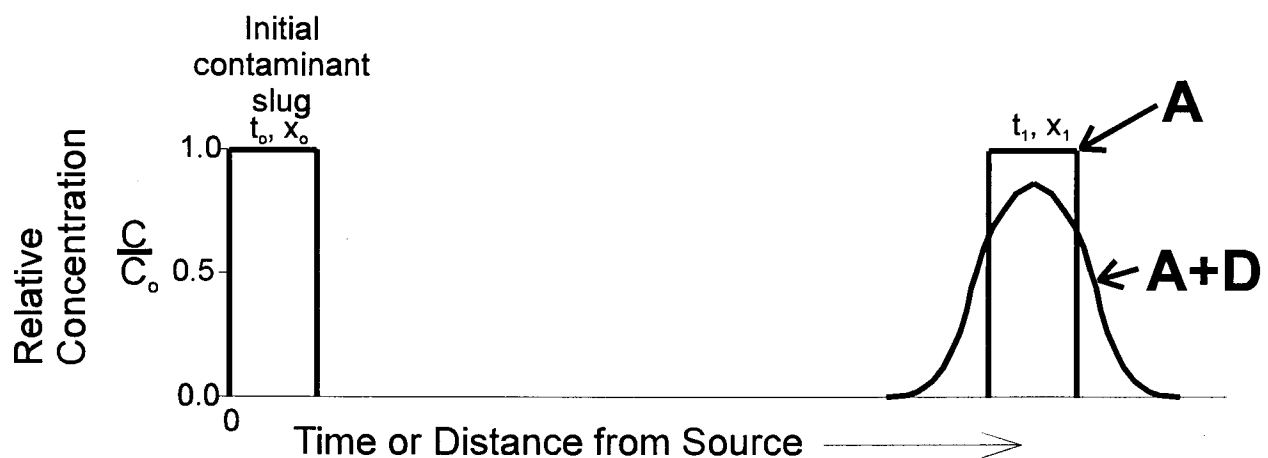
n_e = effective porosity [L^3/L^3]

dH/dL = hydraulic gradient [L/L]

Hydrodynamic Dispersion

- ▶ Longitudinal and Transverse Spreading of Solute Plume
- ▶ Two Components
 - 1) Molecular Diffusion
 - 2) Mechanical Dispersion

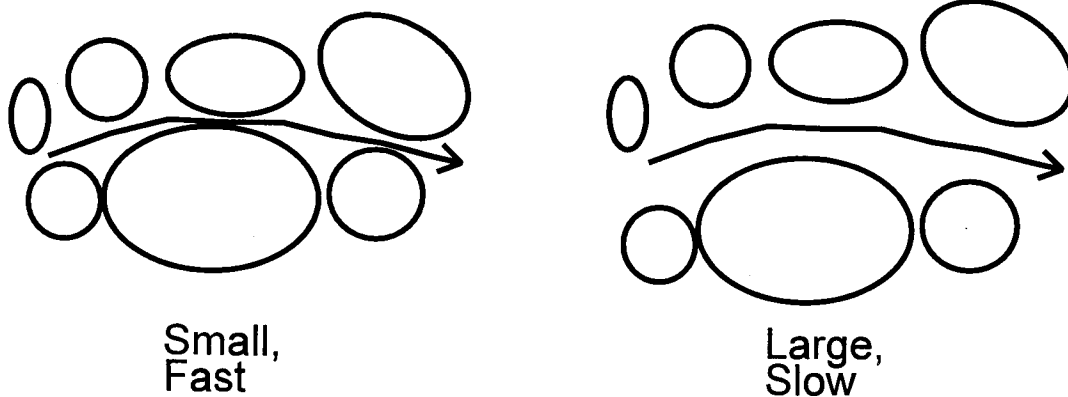
Instantaneous Source with Advection and Dispersion



Mechanical Dispersion

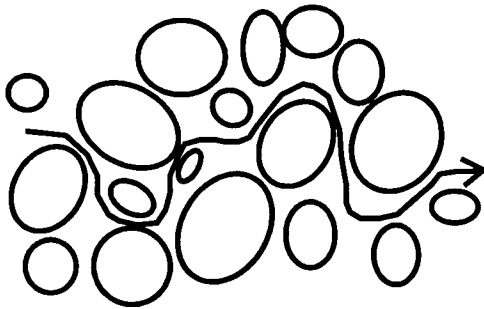
- ▶ Mechanical Mixing
- ▶ Three Mechanisms
 - 1) Variable Pore Size
 - 2) Variable Flow Length (Tortuosity)
 - 3) Pore-Throat Friction

Mechanical Dispersion - Pore Size

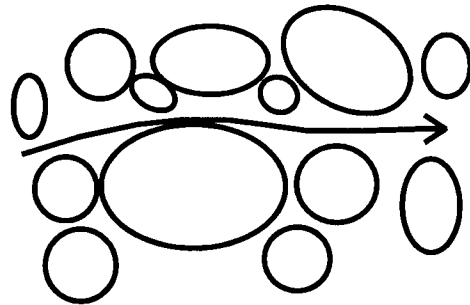


$$Q = vA = \text{Constant}$$

Mechanical Dispersion - Tortuosity

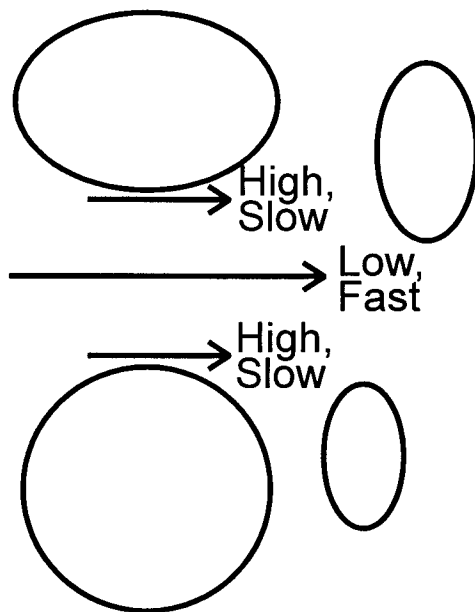


High (Long Flow Path)
Slow

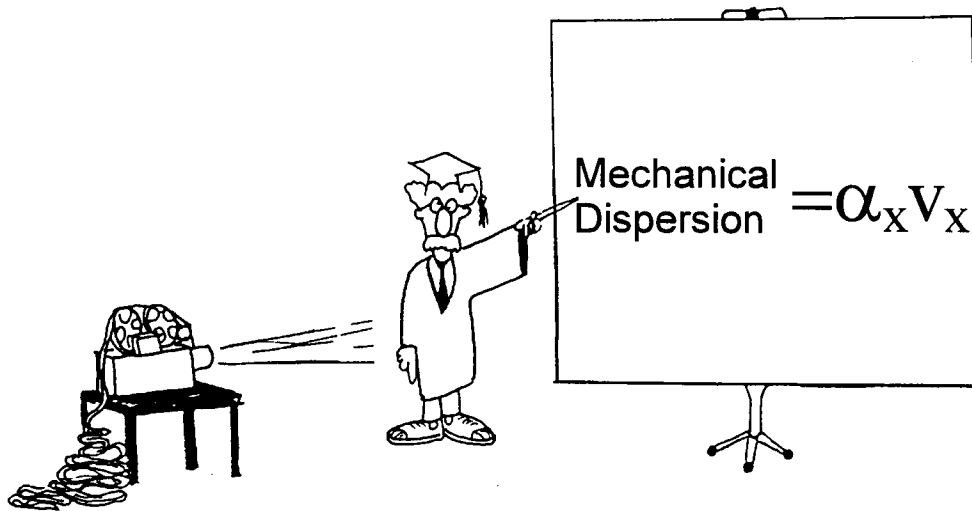


Low (Short Flow Path)
Fast

Mechanical Dispersion - Pore-Throat Friction



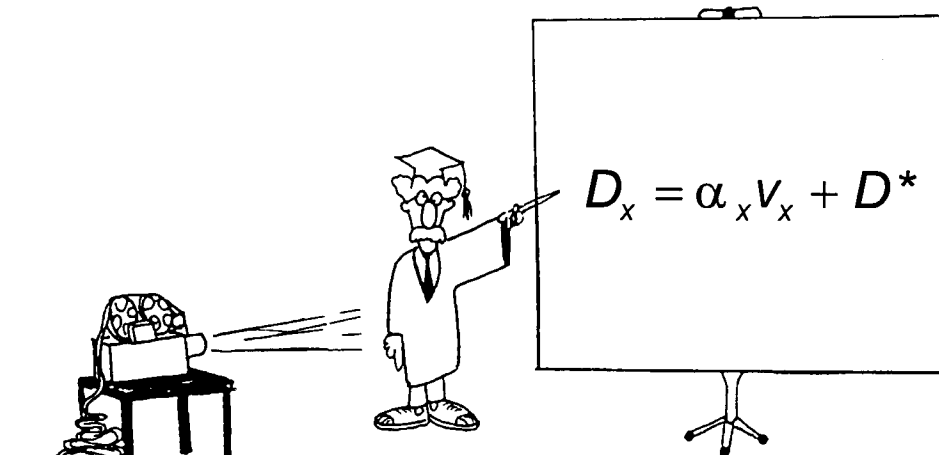
Mechanical Dispersion



α_x = longitudinal dispersivity

v_x = average linear groundwater velocity

Equation of Hydrodynamic Dispersion



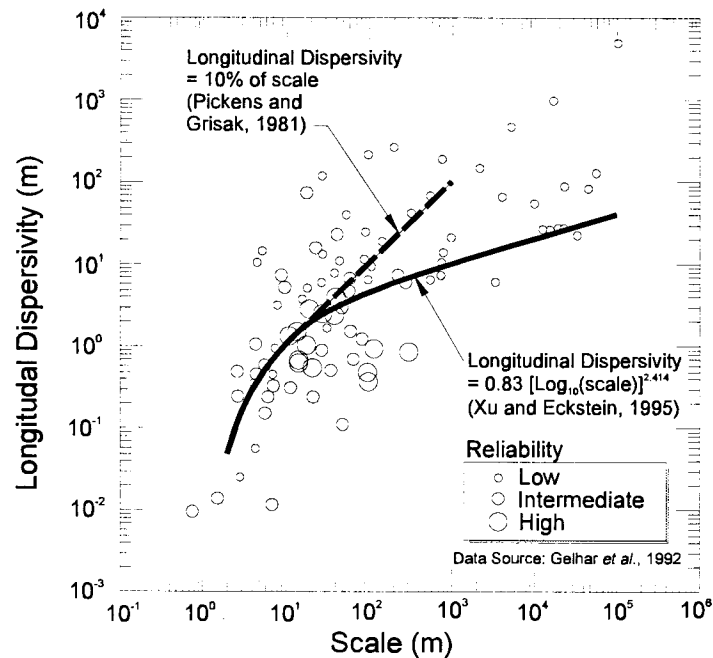
D_x = longitudinal coefficient of hydrodynamic dispersion

α_x = longitudinal dispersivity

v_x = average linear groundwater velocity

D^* = effective molecular diffusion (generally neglected)

Relationship Between Dispersivity and Scale



Source: Newell et al., 1996

Dispersivity Estimate*

$$\alpha_x = 0.83(\text{Log} L_p)^{2.414}$$

α_x = Longitudinal Dispersivity [L]

L_p = Plume Length [L]

*From Xu and Eckstein (1995)

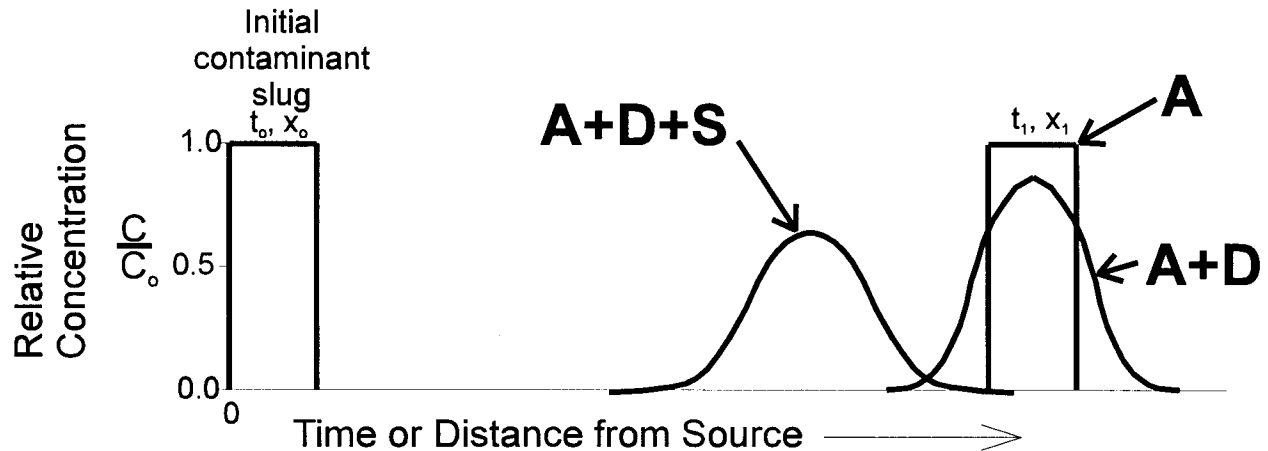
Overview of Adsorption

- ▶ Process Whereby Molecules Become Fixed (Sorbed) To Aquifer Matrix (Hydrophobic Effect)
- ▶ Organic Carbon and Clay Mineral Fractions Generally Act As Sites Of Adsorption (Large SA to V Ratio and Surface Properties)
- ▶ Organic Carbon Fraction most Important If $> 0.1\%$ Of The Aquifer Matrix By Weight

Overview of Adsorption

- ▶ Important Model Input Parameter
- ▶ Causes Slowing (Retardation) of BTEX Relative to Groundwater
- ▶ Quantified Using Coefficient Of Retardation, R
- ▶ Electron Acceptors Sweep Over BTEX Plume
- ▶ Electron Acceptor Depleted "Shadow" Formed Downgradient of BTEX Plume

Instantaneous Source with Advection, Dispersion, and Sorption



Characteristics of Microorganisms

- ▶ Rapid Growth and Metabolism
- ▶ Genetic Plasticity
- ▶ Ability to Adjust Rapidly to a Variety of Environments

Biological Fate of Organic Contaminants

Two Broad Mechanisms

- ▶ Use as a Primary Growth Substrate
 - ▶ Growth-Promoting Biological Oxidation (Electron Donor)
 - ▶ Growth-Promoting Biological Reduction - Halorespiration (Electron Acceptor)
 - ▶ Fermentation
- ▶ Cometabolism
 - ▶ Co-Oxidation
 - ▶ Co-Reduction (Reductive Dechlorination)

Microbially-Mediated Processes of Organic Compound Degradation

- ▶ Aerobic Processes
 - ▶ Aerobic Respiration
 - ▶ Cometabolism (Co-Oxidation)

Microbially-Mediated Processes of Organic Compound Degradation

- ▶ Anaerobic Processes
 - ▶ Denitrification, Manganese (IV) Reduction, Iron (III) Reduction, Sulfate Reduction, Methanogenesis
 - ▶ Halorespiration (Reductive Dechlorination)
 - ▶ Cometabolism (Co-Reduction/ Reductive Dechlorination)

BTEX Biodegradation

- ▶ Numerous Researchers Have Shown That BTEX Biodegrades Via:
 - ▶ Aerobic Respiration
 - ▶ Denitrification
 - ▶ Manganese (IV) Reduction
 - ▶ Iron (III) Reduction
 - ▶ Sulfate Reduction
 - ▶ Methanogenesis

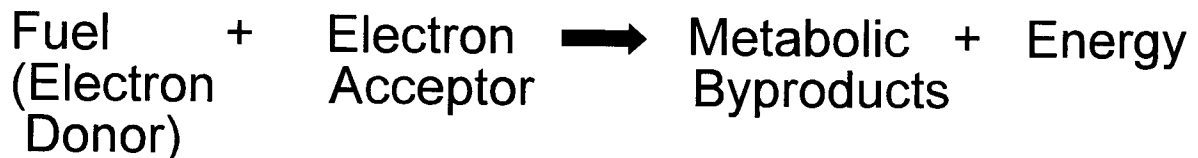
Use of Organic Compound as Primary Growth Substrate

- BTEX Compounds
- Microorganisms Consume Organic Compound to Obtain Energy and Organic Carbon

Mechanisms of Biodegradation

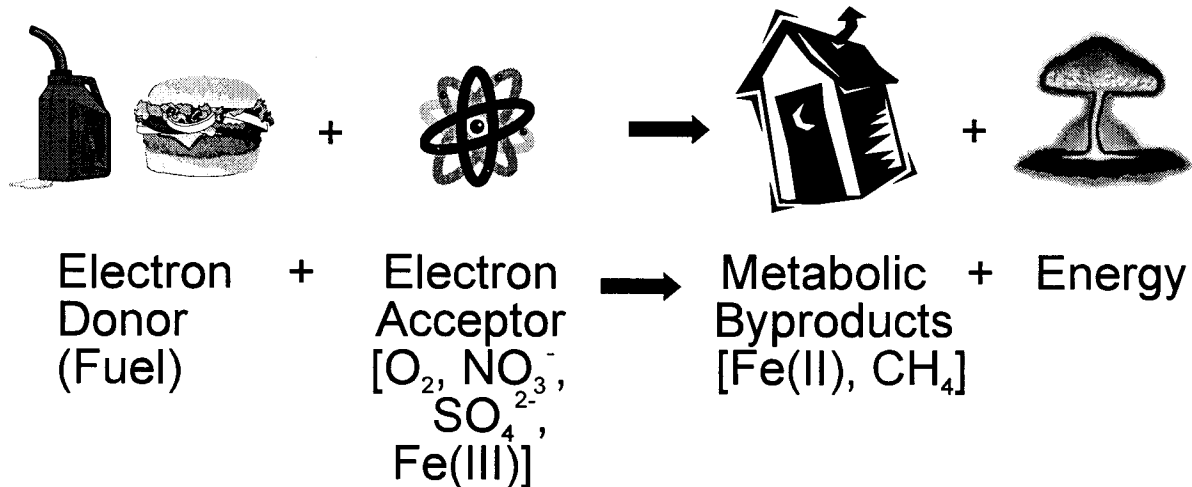
▶ Fuel Hydrocarbons

- ▶ Compounds Used as Electron Donors in Straight Forward Oxidation-Reduction Reactions



- ▶ Reaction will Continue Until all Fuel Hydrocarbons are Depleted

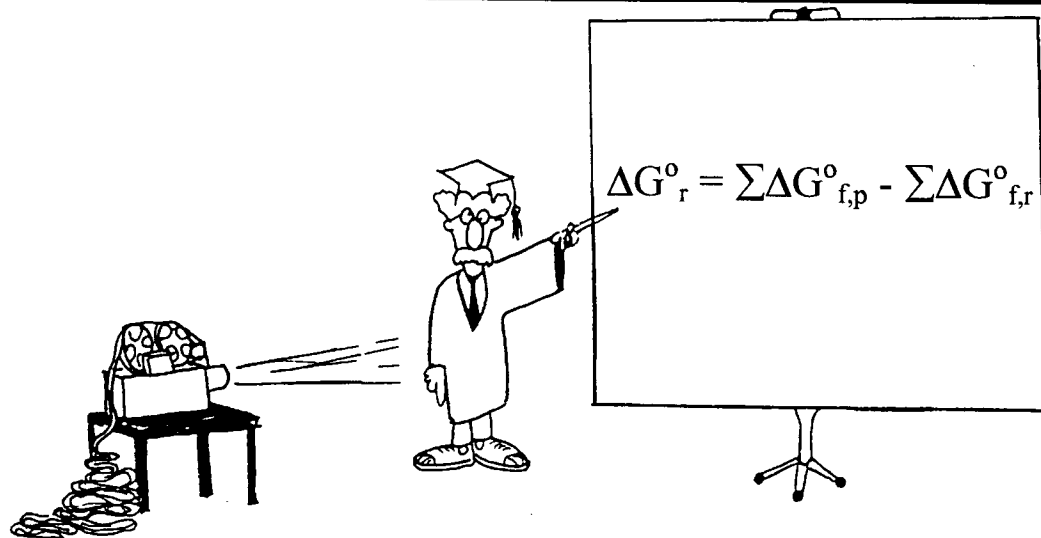
Fuel Hydrocarbon Biodegradation



BTEX Biodegradation via Aerobic Respiration

- ▶ Barker et al., 1987, Natural Attenuation of Aromatic Hydrocarbons in a Shallow Sand Aquifer: GWMR Winter 1987:64-71. (B,T,X)
- ▶ Thomas et al., 1990, Biodegradation of BTEX in subsurface materials contaminated with gasoline: Water Science Technology 22:53-62. (B,T,E,X)

Gibb's Free Energy Calculation



Where: ΔG_r = Gibb's Free Energy of the Reaction at Standard State

$\Delta G_{f,p}$ = Gibb's Free Energy of Formation for Products at Standard State

$\Delta G_{f,r}$ = Gibb's Free Energy of Formation for the Reactants at Standard State

Benzene Oxidation/Aerobic Respiration



$$\Delta G^{\circ}_r = -3566 \text{ kJ/mole Benzene}$$

Mass Ratio of O_2 to C_6H_6 = 3.1:1

0.32 mg/L C_6H_6 Degraded per mg/L O_2 Consumed

BTEX Biodegradation via Denitrification

- ▶ Evans et al., 1991, Degradation of toluene and m-xylene and transformation of o-xylene by denitrifying enrichment cultures: Appl. Environ. Microbiol., 57:450-454. (T,X)
- ▶ Major et al., 1988, Biotransformation of benzene by denitrification in aquifer sand: Ground Water 26:8-14. (B)

BTEX Biodegradation via Denitrification

- ▶ Hutchins et al., 1991, Biodegradation of Aromatic Hydrocarbons by Aquifer Microorganisms Under Denitrifying Conditions: Environ. Sci. Technol., 25:68-76. (B,T,E,X)

Benzene Oxidation/Denitrification



$$\Delta G_r^0 = -3245 \text{ kJ/mole Benzene}$$

Mass Ratio of NO_3^- to C_6H_6 = 4.8:1

0.2 mg C_6H_6 Degraded per mg NO_3^- Consumed

BTEX Biodegradation via Iron (III) Reduction

- ▶ Lovley et al., 1989, Oxidation of Aromatic Contaminants Coupled to Microbial Iron Reduction: Nature 339:297-300. (T)
- ▶ Lovley et al., 1994, Stimulated Anoxic Biodegradation of Aromatic Hydrocarbons Using Fe(III) Ligands: Nature 370:128-131. (B)

Benzene Oxidation/Iron Reduction



$$\Delta G_r^0 = -2343 \text{ kJ/mole Benzene}$$

Mass Ratio of $\text{Fe}(\text{OH})_3$ to C_6H_6 = 41:1

Mass Ratio of Fe^{2+} Produced to C_6H_6 Degraded = 15.7:1

0.06 mg C_6H_6 Degraded per mg Fe^{2+} Produced

BTEX Biodegradation via Sulfate Reduction

- ▶ Lovley et al., 1995, Benzene Oxidation Coupled to Sulfate Reduction: Appl. & Env. Micro., v. 61, no. 3, p. 953-958. (B)
- ▶ Thierrin et al., 1995, A Ground-Water Tracer Test with Deuterated Compounds for Monitoring In Situ Biodegradation and Retardation of Aromatic Hydrocarbons: Ground Water, v. 33, no. 3, p. 469-475. (T,X,Napthalene)

Benzene Oxidation/Sulfate Reduction



$$\Delta G_r^0 = -340 \text{ kJ/mole Benzene}$$

Mass Ratio of SO_4^{2-} to C_6H_6 = 4.6:1

0.22 mg C_6H_6 Degraded per mg Sulfate Consumed

BTEX Biodegradation via Methanogenesis

- ▶ Grbic-Galic and Vogel, 1987, Transformation of Toluene and Benzene by mixed Methanogenic Cultures: Appl. Environ. Microbiol., 53:254-260. (B,T)
- ▶ Thierrin et al., 1995, A Ground-Water Tracer Test with Deuterated Compounds for Monitoring In Situ Biodegradation and Retardation of Aromatic Hydrocarbons: Ground Water, v. 33, no. 3, p. 469-475. (T,X,Napthalene)

BTEX Biodegradation via Methanogenesis

- ▶ Wilson et al., 1986, Biotransformations of Selected Alkylbenzenes and Halogenated Aliphatic Hydrocarbons in Methanogenic Aquifer Material: A Microcosm Study: Environ. Sci. Technol., 20:997-1002. (B,T,E,X)

Benzene Oxidation/Methanogenesis

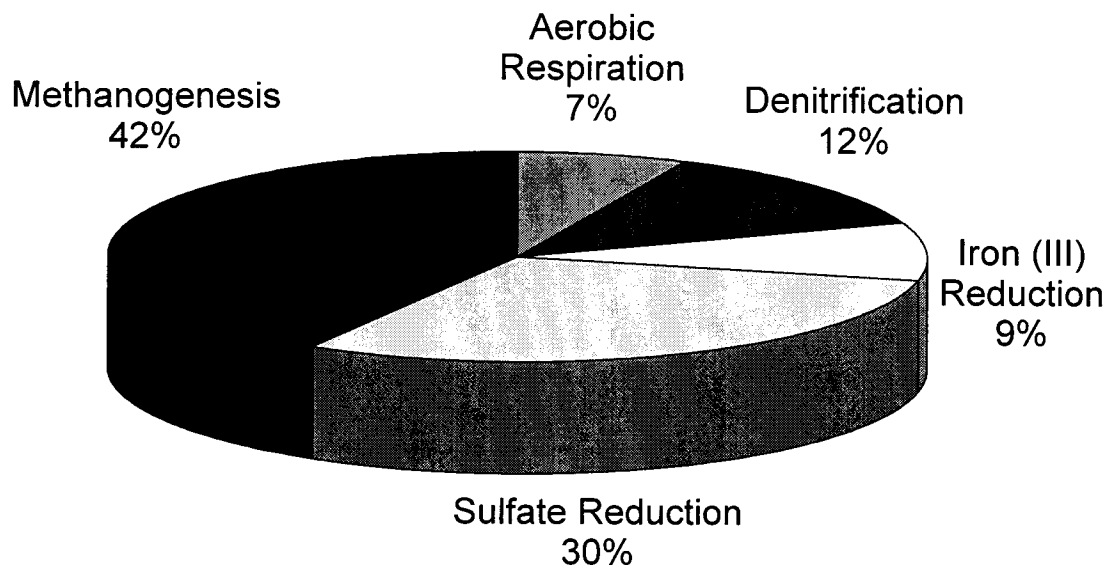


$$\Delta G_r^0 = -135.6 \text{ kJ/mole Benzene}$$

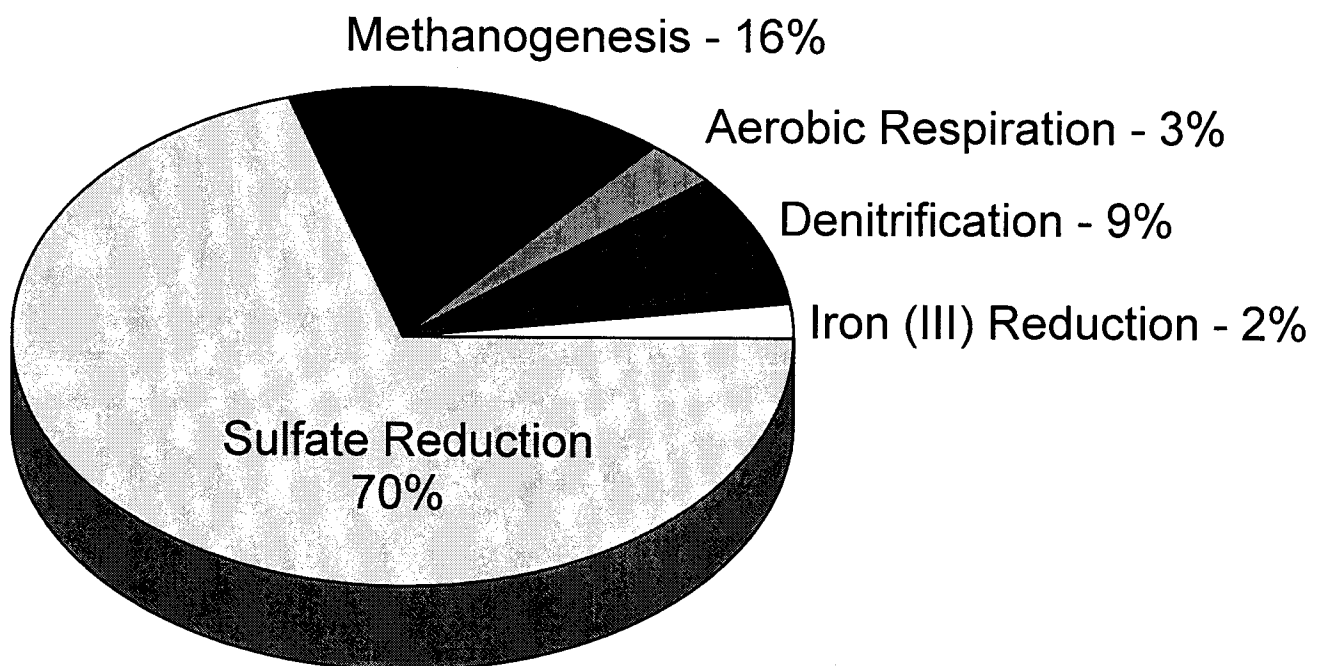
Mass Ratio CH_4 Produced to C_6H_6 Degraded = 0.8:1

1.25 mg C_6H_6 Degraded per mg CH_4 Produced

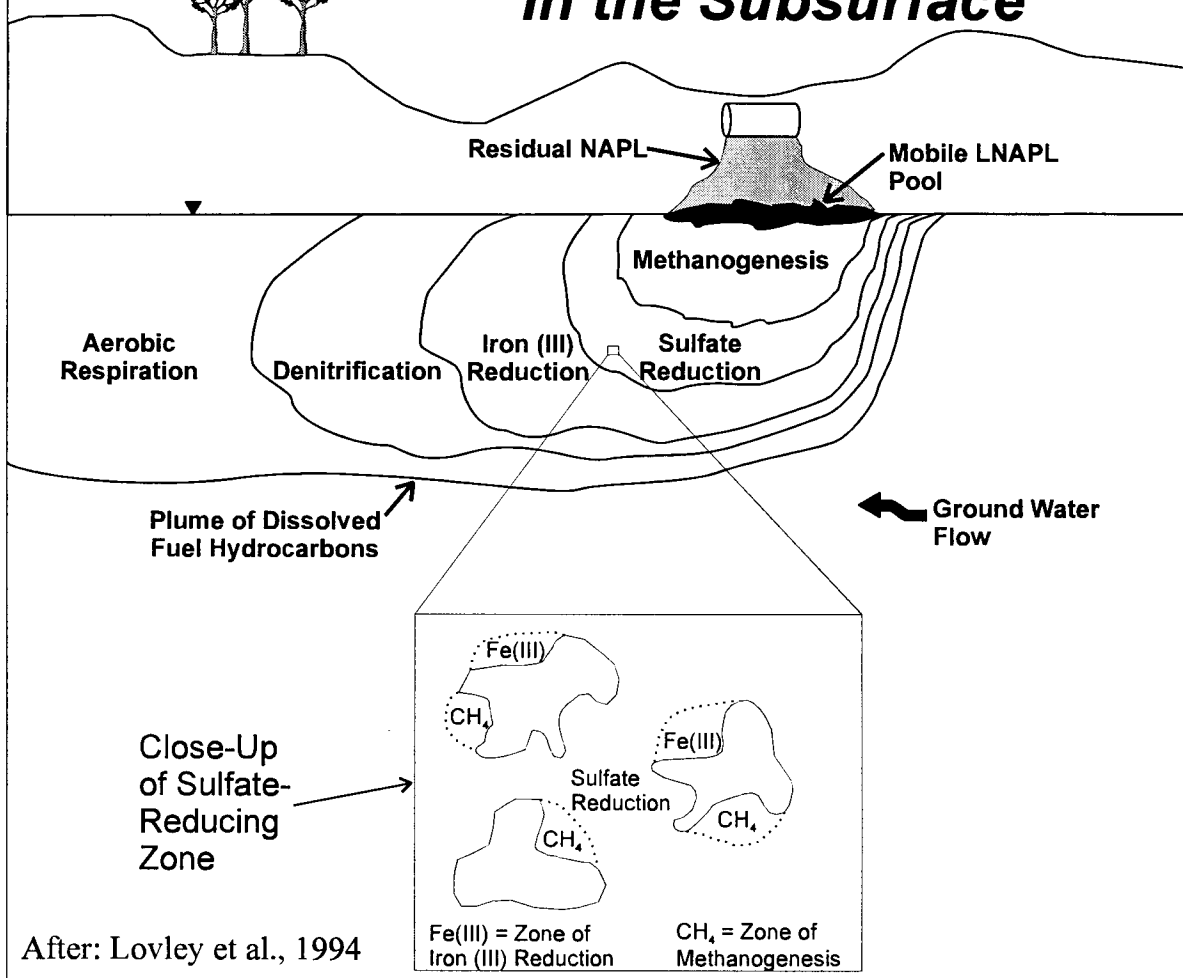
Relative Importance of Biodegradation Mechanisms at 25 Sites



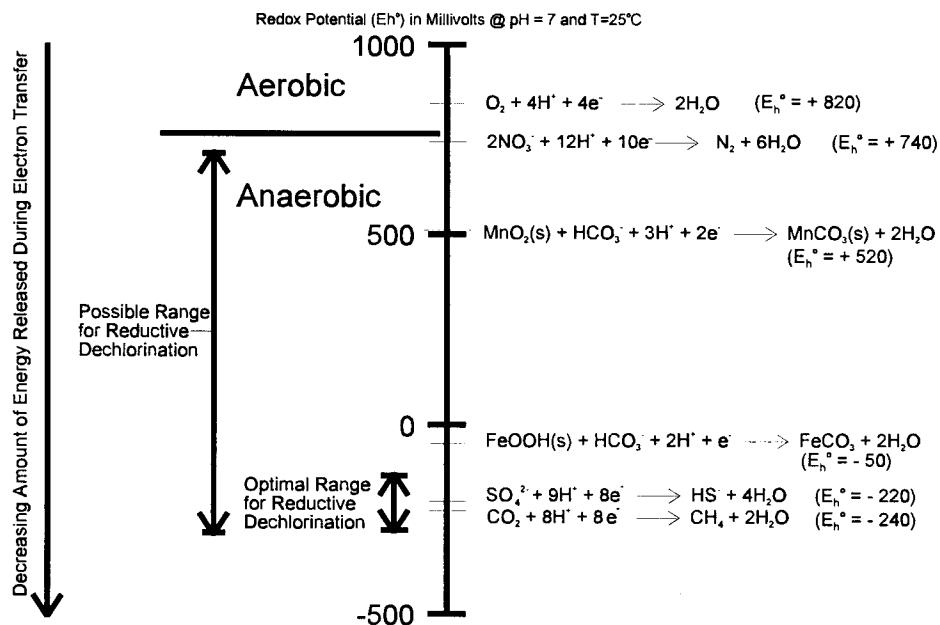
Relative Importance of BTEX Biodegradation Mechanisms Based on Expressed Assimilative Capacity



Conceptualization of Electron Acceptor Zones in the Subsurface



Redox Potential (E_h°)



Modified From Bouwer (1994)

Chlorinated Solvent Biodegradation

- ▶ Numerous Researchers Have Shown That Chlorinated Solvents Biodegrade Via:
 - ▶ Aerobic Respiration (DCE, VC, Chlorobenzenes)
 - ▶ Iron (III) Reduction (VC)
 - ▶ Halorespiration (PCE, TCE, DCE)
 - ▶ Cometabolism (TCE)

Mechanisms of Biodegradation

- ▶ Chlorinated Solvents
 - ▶ Compounds can be used as Electron Donors or Electron Acceptors, or can be degraded via Cometabolism

Reductive Dechlorination (Halorespiration)

Reductive Dechlorination is the only Biological Mechanism known to degrade the common Chlorinated Solvents (PCE, TCE, TCA, and CT) in Most Groundwater Systems

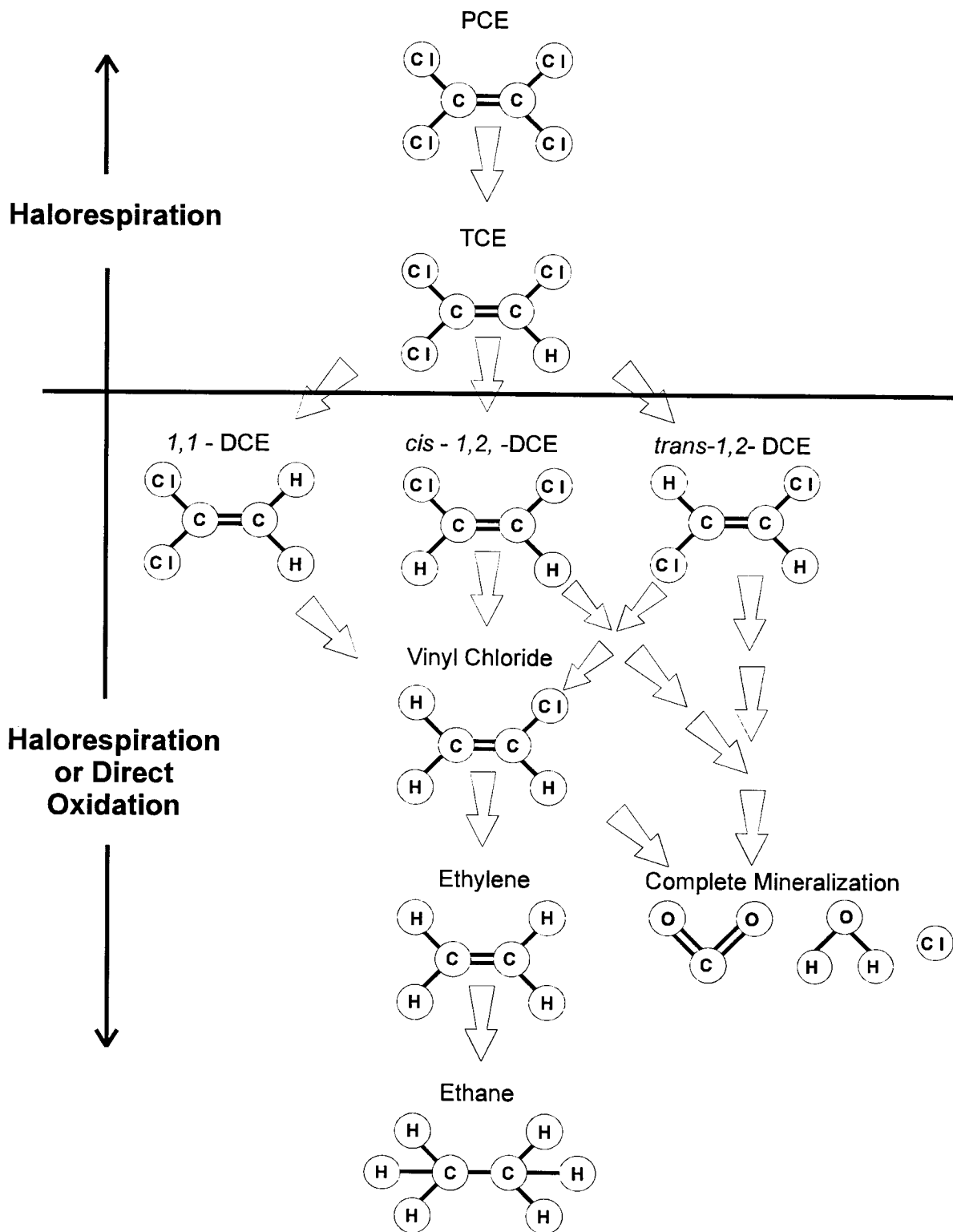
Requirements for Reductive Dechlorination

- ▶ Halorespiring Bacteria
- ▶ Electron Donor (for Carbon and Hydrogen)
- ▶ Strongly Reducing Conditions (Sulfate-Reducing or Methanogenic)
- ▶ Hydrogen at Concentrations $> 1\text{nM}$

Requirements for Reductive Dechlorination

- ▶ Primary Substrate
 - ▶ Native Organic Carbon, BTEX, Landfill Leachate, etc.
- ▶ Strongly Reducing Conditions
 - ▶ Generally Need Methanogenic Conditions

Degradation Mechanisms for Chlorinated Solvents



Foot Race for Hydrogen

- ▶ Reductive Dechlorination is in a “Foot Race” with Competing Donor Uses

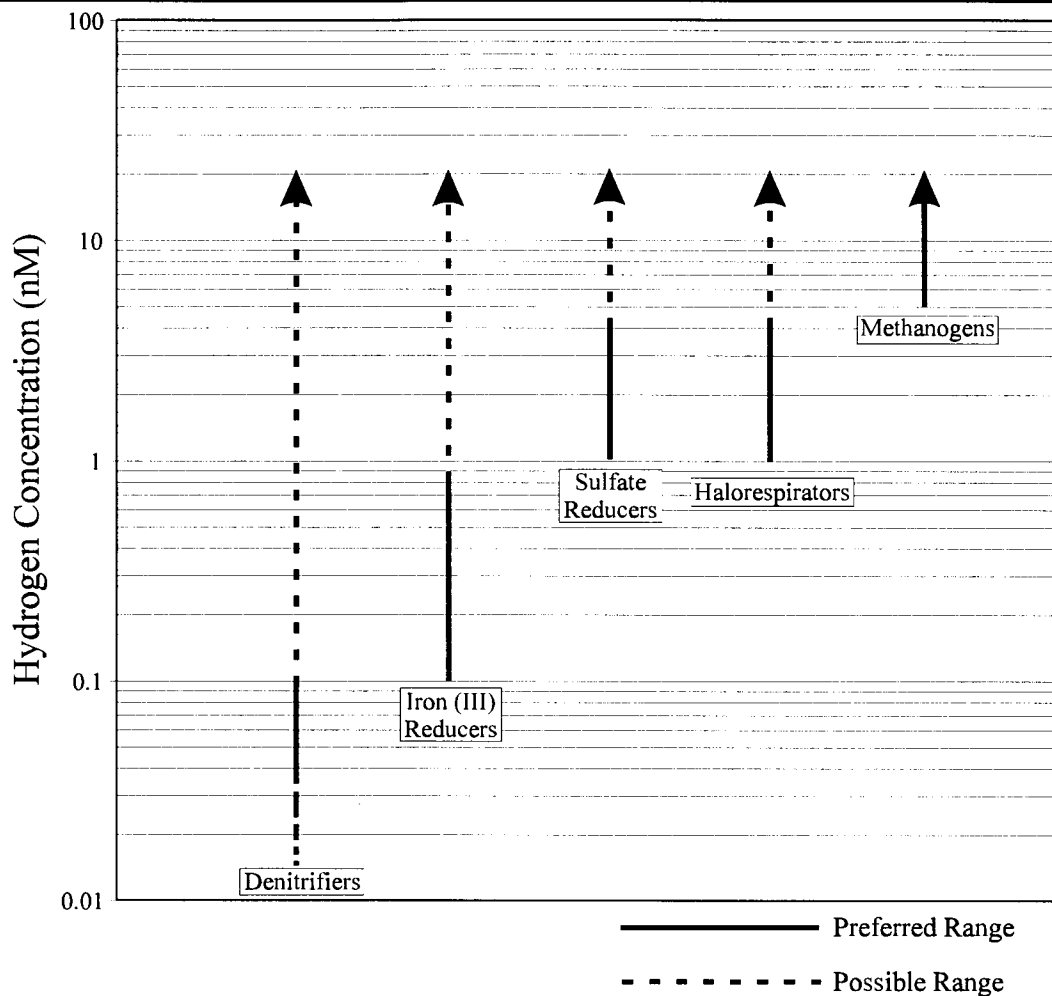
-Gossett & Zinder, 1996, EPA/540/R-96/509

- ➔ If Too Little Electron Donor is Present then not Enough H_2 is Produced to Sustain Reductive Dechlorination
- ➔ If Too Much Electron Donor is Present there may be Too Much Competition

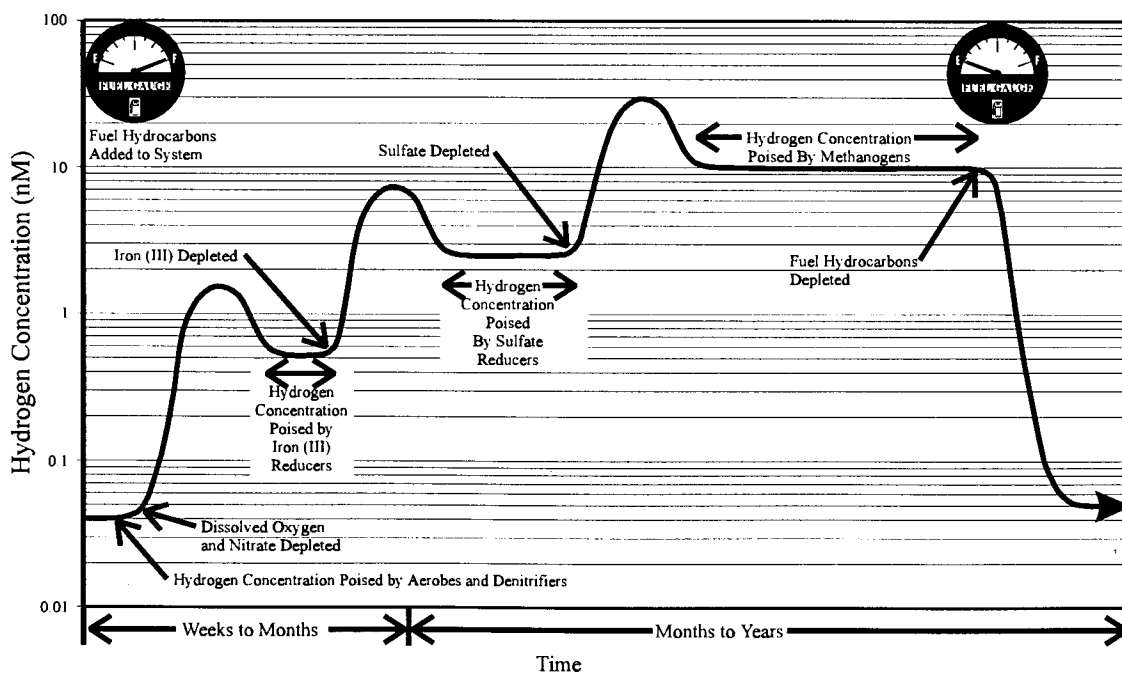
Competition for Hydrogen

- ▶ Sulfate Reducers, Methanogens, and Dechlorinators Compete for Hydrogen in Subsurface Environments
- ▶ Methanogens Do Not Come Into Play Until Hydrogen Concentrations are $> 5nM$
- ▶ Thermodynamic Arguments Suggest That Halorespirators Will Out-Compete Sulfate Reducers (Not Certain)

Range of Hydrogen Concentrations



Hydrogen Concentrations over Time



Behavior of Chlorinated Solvent Plumes

- ▶ Type 1 Behavior
 - ▶ Primary Substrate is Anthropogenic Organic Carbon
 - ▶ Solvent Plume Degrades
- ▶ Type 2 Behavior
 - ▶ Primary Substrate is Native Organic Carbon
 - ▶ Solvent Plume Degrades
- ▶ Type 3 Behavior
 - ▶ Low Native Organic Carbon Concentrations
 - ▶ Low Anthropogenic Carbon Concentrations
 - ▶ PCE, TCE, and DCE? do not Degrade

Type 1 Behavior

- ▶ Primary Substrate is Anthropogenic Carbon
 - ▶ BTEX, Landfill Leachate, etc.
- ▶ Anthropogenic Carbon Drives Dechlorination
- ▶ Questions
 - ▶ Does Electron Acceptor Supply Exceed Demand? (i.e., is electron acceptor supply adequate?)
 - ▶ Will Plume Strangle Before it Starves?
 - ▶ What is Role of Competing Electron Acceptors?
 - ▶ Do PCE, TCE, and DCE Dechlorinate?
 - ▶ Is Vinyl Chloride Oxidized?
 - ▶ Is Biodegradation Rate Adequate?

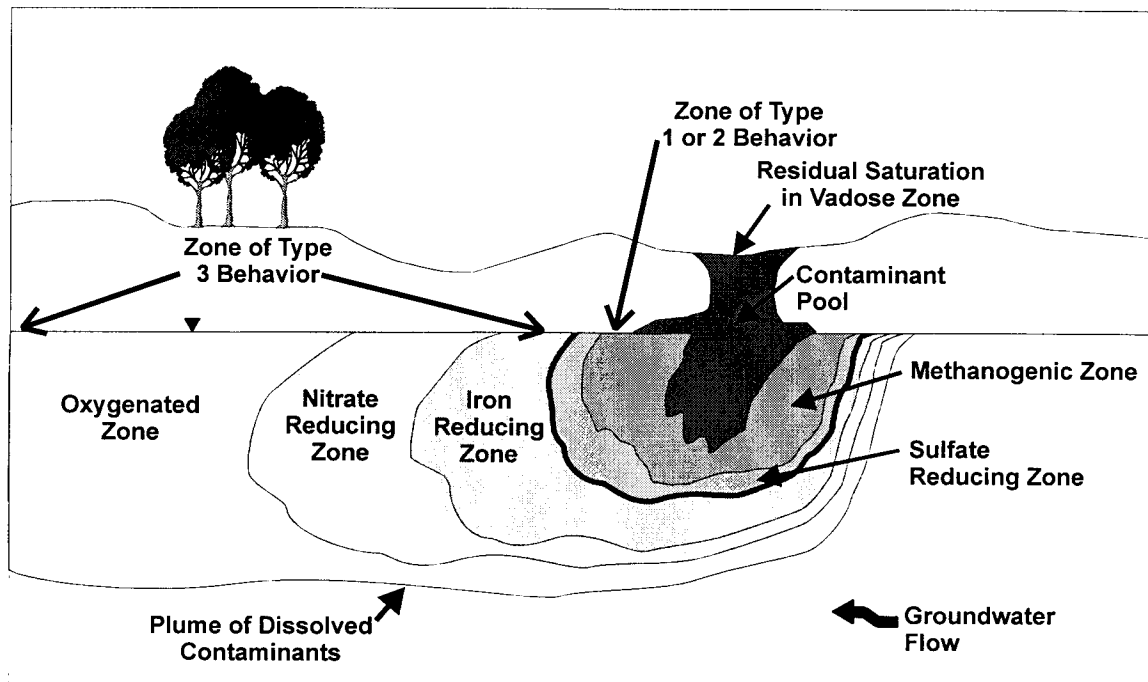
Type 2 Behavior

- ▶ Primary Substrate is Native Organic Carbon
- ▶ Native Organic Carbon Drives Dechlorination
- ▶ Questions
 - ▶ Does Electron Acceptor Supply Exceed Demand? (i.e., is electron acceptor supply adequate?)
 - ▶ Will Plume Strangle Before it Starves?
 - ▶ What is Role of Competing Electron Acceptors?
 - ▶ Do PCE, TCE, and DCE Dechlorinate?
 - ▶ Is Vinyl Chloride Oxidized?
 - ▶ Is Biodegradation Rate Adequate?

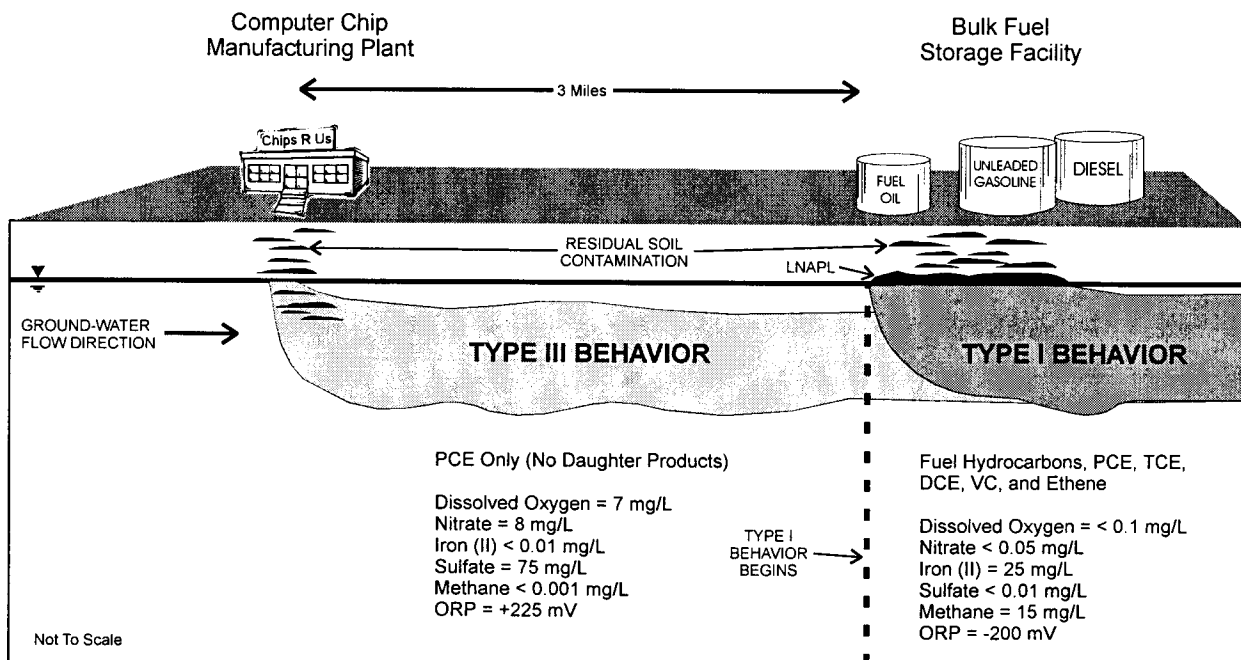
Type 3 Behavior

- ▶ Low Native Organic Carbon Concentrations
- ▶ Low Anthropogenic Carbon Concentrations
- ▶ Dissolved Oxygen (and Nitrate) Concentration(s) Greater than 1.0 mg/L (Oxygenated System)
- ▶ Reductive Dechlorination Will Not Occur
Highly Halogenated Compounds Such
As PCE and TCE Will Not Degrade
- ▶ DCE and VC May be Oxidized

Conceptualization of Electron Acceptor Zones in the Subsurface



Conceptual Site Model Type III to Type I Behavior



Differences Between BTEX and Chlorinated Solvent Plumes

- ▶ BTEX Biodegradation Will Always Proceed To Completion
- ▶ Chlorinated Solvent Biodegradation Dependent Upon Many Factors
- ▶ Chlorinated Solvent Plume Could Run Out Of Primary Substrate Before Reductive Dechlorination Is Complete

Three Lines of Evidence Used To Document Natural Attenuation

- 1) Historical Database Showing Plume Stabilization and/or Loss of Contaminant Mass Over Time
- 2) Contaminant and Geochemical Analytical Data
- 3) Microbiological Laboratory Data

Site Characterization

Adequate Site Characterization
Is The Single Most Important Step
In The Intrinsic Remediation
Demonstration

Soil Analytical Protocol

- ▶ Chlorinated Solvents
- ▶ Aromatic Hydrocarbons
- ▶ Total Organic Carbon
- ▶ Bulk Density

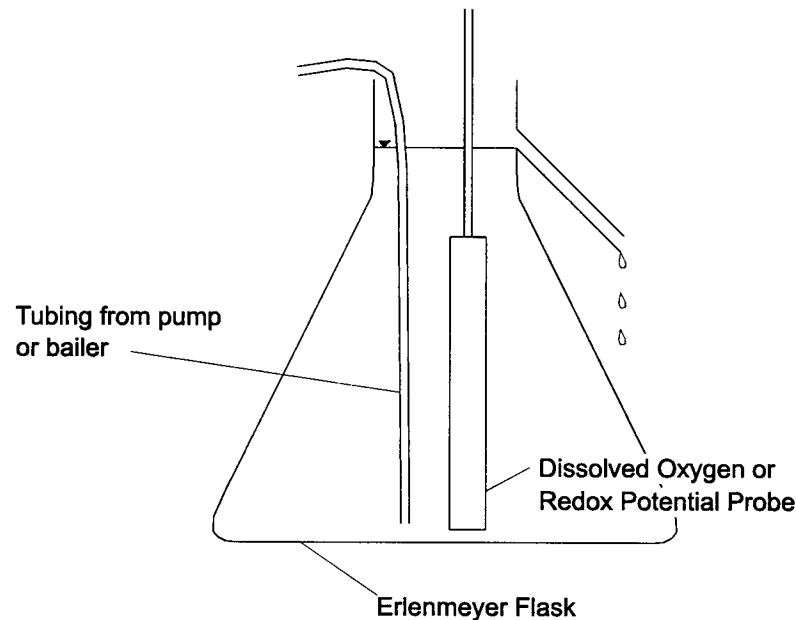
Groundwater Analytical Protocol - BTEX

- | | |
|---|-------------------|
| ▶ Aromatic Hydrocarbons | ▶ Redox Potential |
| ▶ TPH | ▶ Alkalinity |
| ▶ Dissolved Oxygen | ▶ pH |
| ▶ Nitrate | ▶ Temperature |
| ▶ Ferrous Iron | |
| ▶ Sulfate | |
| ▶ Methane | |
| ▶ Compounds Required
for Regulatory Compliance | |

Groundwater Analytical Protocol - Solvents

- | | |
|-------------------------|----------------------------|
| ▶ VOC Analysis (SW8260) | ▶ Dissolved Organic Carbon |
| ▶ Dissolved Oxygen | |
| ▶ Nitrate | ▶ Redox Potential |
| ▶ Iron (II) | ▶ Alkalinity |
| ▶ Sulfate | ▶ pH |
| ▶ Methane/Ethane/Ethene | ▶ Temperature |
| ▶ Chloride | |
| ▶ Hydrogen (Optional) | |

Oxygen and Redox Potential Sampling



Document Occurrence of Natural Attenuation - Three Lines of Evidence

- 1** Documented Loss of Contaminants at the Field Scale
- 2** Contaminant and Geochemical Analytical Data
- 3** Microbiological Laboratory Data

Document Occurrence of Intrinsic Bioremediation

- ▶ Use at Least Two of the Three Lines of Evidence (Preferably First Two Lines)
 - ▶ Historical Database Showing Plume Stabilization and/or Loss of Contaminant Mass Over Time
 - ▶ Contaminant and Geochemical Analytical Data
 - ▶ Microbiological Laboratory Data

Weight of Evidence

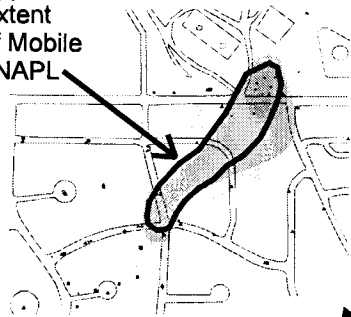
- ▶ Independent and Converging Lines of Evidence Should Be Used To Document Natural Attenuation

Documented Loss of Contaminant Mass

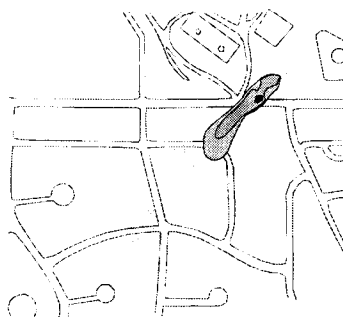
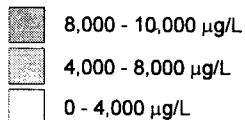
- ▶ Statistically Significant Historical Database Showing Plume Stabilization and/or Loss of Contaminant Mass
 - ▶ Contaminant Concentrations in Space
 - ▶ Contaminant Concentrations Over Time

TOTAL BTEX - HILL AFB Large POL Facility - Up to 8 Feet of Mobile LNAPL

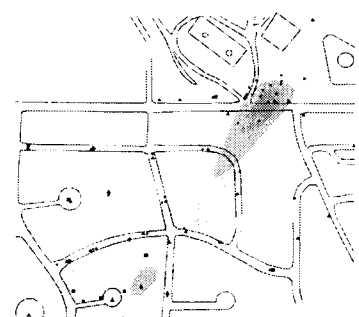
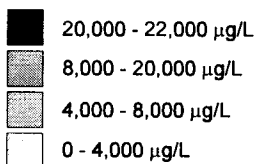
Approximate
Extent
of Mobile
LNAPL



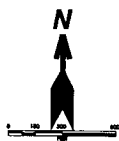
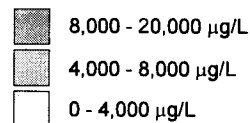
AUGUST 1993



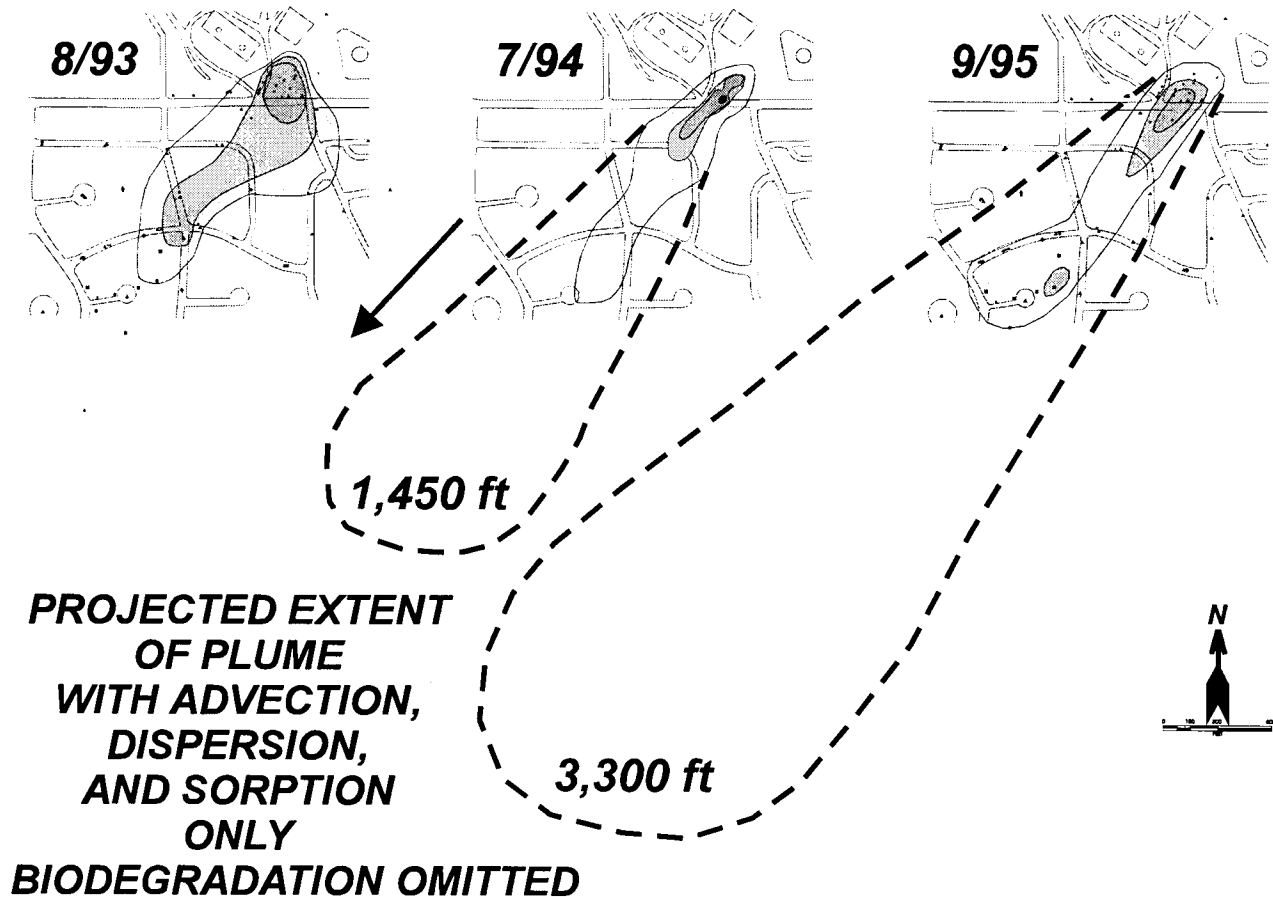
JULY 1994



SEPTEMBER 1995



Projected Extent Of BTEX - Hill AFB



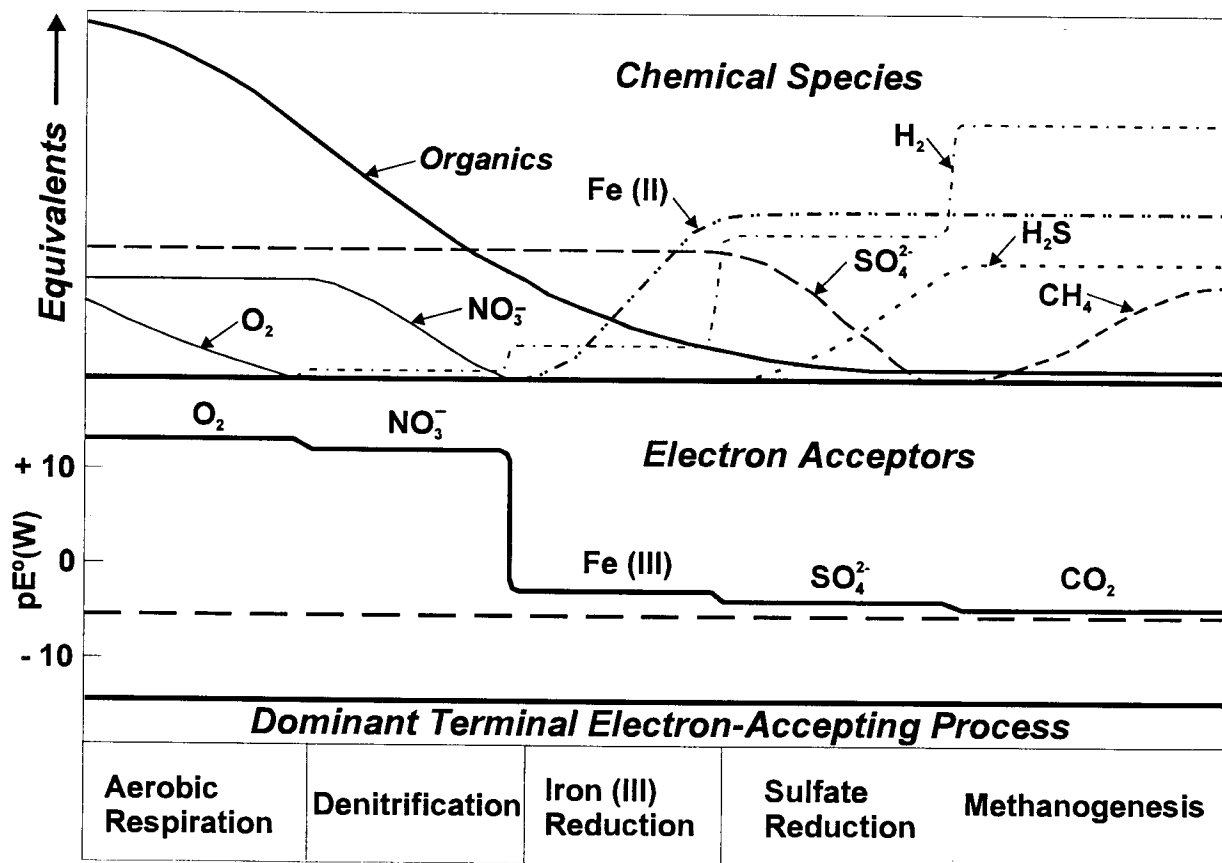
Chemical and Geochemical Data Including

- ▶ Depletion of Electron Acceptors and Donors
- ▶ Increasing Metabolic Byproduct Concentrations
- ▶ Decreasing Parent Compound Concentrations
- ▶ Increasing Daughter Compound Concentrations

Chemical Evidence of Biodegradation

- ▶ Areas With Contamination Show:
 - ▶ Highly Elevated Methane Concentrations
 - ▶ Elevated Iron (II) Concentrations
 - ▶ Elevated Chloride Concentrations
 - ▶ Lowered Oxidation-Reduction Potential
 - ▶ Daughter Products
 - *cis*-1,2-DCE > *trans*-1,2-DCE or 1,1-DCE
 - VC is Present

Geochemical Evolution of Ground Water

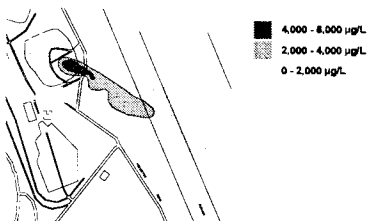


After: Bouwer and McCarthy, 1984

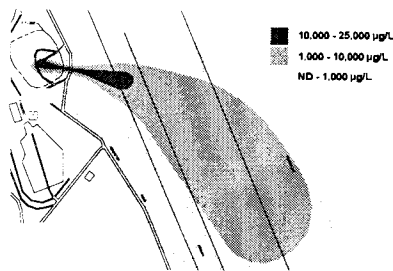
Time →
← Distance From Source

Chlorinated Solvents & Byproducts

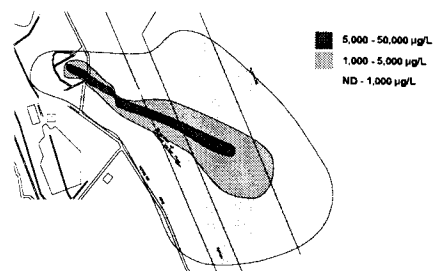
TOTAL BTEX



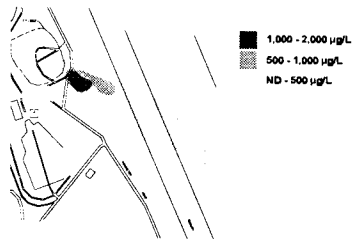
TRICHLOROETHENE



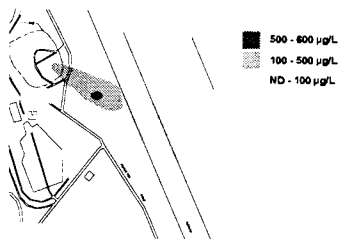
DICHLOROETHENE



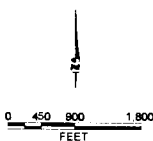
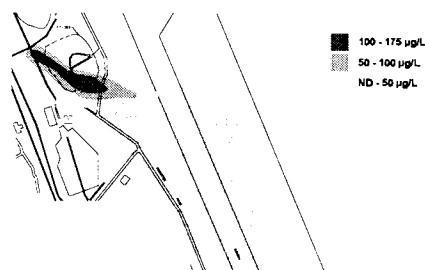
VINYL CHLORIDE



ETHENE

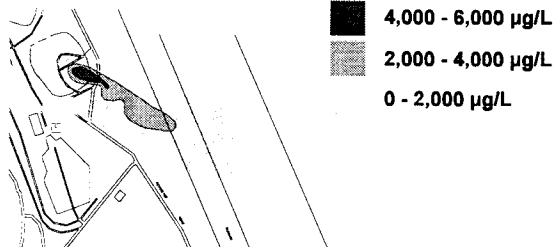


CHLORIDE

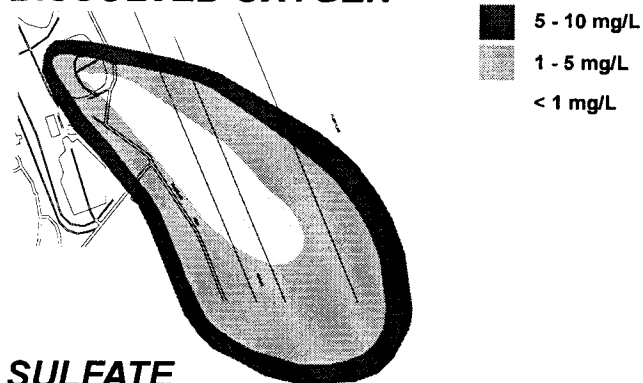


BTEX and Electron Acceptors

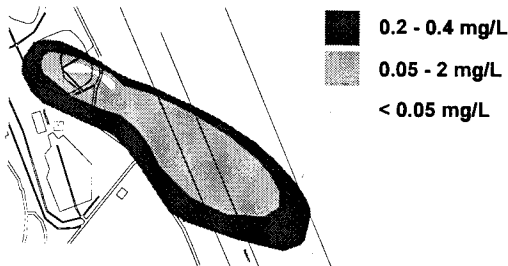
TOTAL BTEX



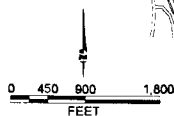
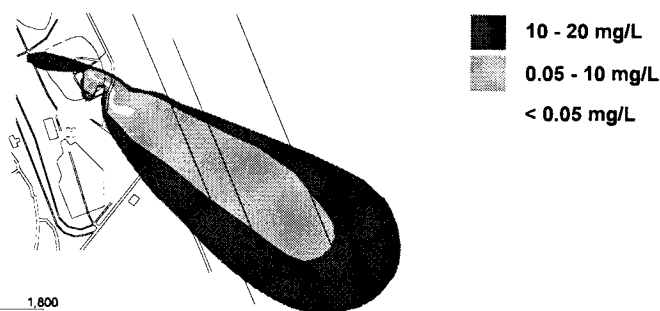
DISSOLVED OXYGEN



NITRATE

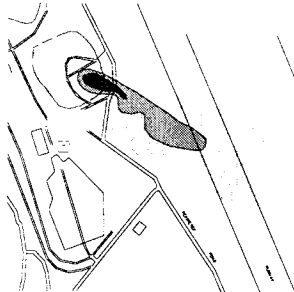


SULFATE



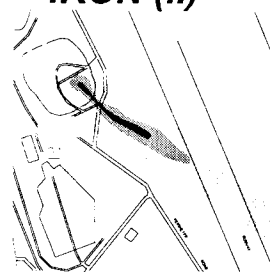
BTEX and Metabolic Byproducts

TOTAL BTEX



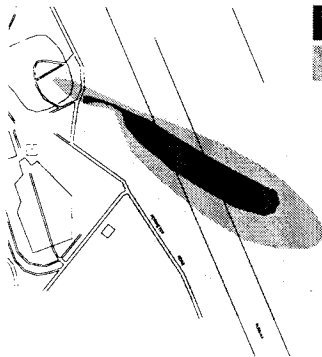
4,000 - 6,000 µg/L
 2,000 - 4,000 µg/L
 0 - 2,000 µg/L

IRON (II)



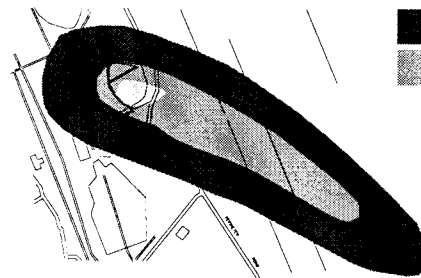
10 - 11 mg/L
 5 - 10 mg/L
 0.05 - 5 mg/L

METHANE

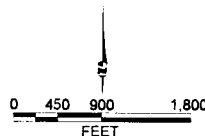


> 0.5 mg/L
 0.3 - 0.5 mg/L
 0 - 0.3 mg/L

pe



4 - 7
 2 - 4
 < 2



Trends During Biodegradation

Plattsburgh Air Force Base

ANALYTE	UPGRADIENT (mg/L)	PLUME INTERIOR (mg/L)
Oxygen	11	<0.1
Nitrate	0.5	<0.05
Iron (III)	0.0	46
Sulfate	25	<0.05
Methane	<0.001	3.5
Chloride	2	82
Ethene	<0.001	0.182
Hydrogen	0.0	11 nM

Microbiological Laboratory Data

- ▶ Microcosm Studies
- ▶ Microbial Cell Enumeration
(Plate Counts, Petroleum Degradation)
- ▶ Dehydrogenase Activity Test

Laboratory Studies

- ▶ Should Be Used Very Selectively In Assessing
the Efficiency of Natural Attenuation

Screening for Natural Attenuation of Petroleum Hydrocarbons

- ▶ Seven Simple Steps

Screening for Natural Attenuation of Petroleum Hydrocarbons

- ▶ Seven Simple Steps

Screening for Natural Attenuation of Petroleum Hydrocarbons

- 1) Place Enough Monitoring Wells To Delineate The Lateral and Vertical Extent of Ground-Water Contamination and Determine the Distribution of Hydrostratigraphic Units

Screening for Natural Attenuation of Petroleum Hydrocarbons - Con't

- 2) ► Measure Water Levels in the Wells
 - Prepare a Potentiometric Map
 - Determine Hydraulic Gradient
 - Perform Slug Tests or Pumping Tests to Determine the Distribution of Hydraulic Conductivity

Screening for Natural Attenuation of Petroleum Hydrocarbons - Con't

- 3) Measure Concentrations of Geochemical Indicator Parameters

Screening for Natural Attenuation of Petroleum Hydrocarbons - Con't

- 4) Estimate Biodegradation Rates

Screening for Natural Attenuation of Petroleum Hydrocarbons - Con't

- 5) Using the Results of Steps 1,2, and 4,
Compare Rate of Contaminant Transport
to Rate of Biodegradation

Screening for Natural Attenuation of Petroleum Hydrocarbons - Con't

- 6) Evaluate the Efficiency of Natural Attenuation

Screening for Natural Attenuation of Petroleum Hydrocarbons - Con't

7) Evaluate Potential Receptor Impacts

Screening for Natural Attenuation of Chlorinated Solvents

► Eight Simple Steps

Screening for Natural Attenuation of Chlorinated Solvents - Con't

- 1) Place Sufficient PVC-cased Monitoring Wells At The Site To Delineate The Areal and Vertical Extent of Ground-Water Contamination And Determine the Distribution of Hydrostatigraphic Units

Screening for Natural Attenuation of Chlorinated Solvents - Con't

- 2) ► Measure Water Levels in the Wells
 - Prepare a Potentiometric Map
 - Determine Hydraulic Gradient
 - Perform Slug Tests or Pumping Tests to Determine the Distribution of Hydraulic Conductivity

Screening for Natural Attenuation of Chlorinated Solvents - Con't

- 3) Measure Concentrations of Indicator Parameters

Screening for Natural Attenuation of Chlorinated Solvents - Con't

- 4) Using the Results of Step 3 to Deduce the Distribution of Ambient Redox Processes at the Site

Screening for Natural Attenuation of Chlorinated Solvents - Con't

- 5) Categorize the Site According to the Progression of Redox Processes

Screening for Natural Attenuation of Chlorinated Solvents - Con't

- 6) Deduce the Efficiency of Natural Attenuation According to the Progression of Redox Conditions, Mass Loss of Solvent Concentrations, and the Production/Destruction of Daughter Products

Screening for Natural Attenuation of Chlorinated Solvents - Con't

- 7) Evaluate Efficiency of Natural Attenuation
in the Context of Contaminant Transport to
Sensitive Receptors

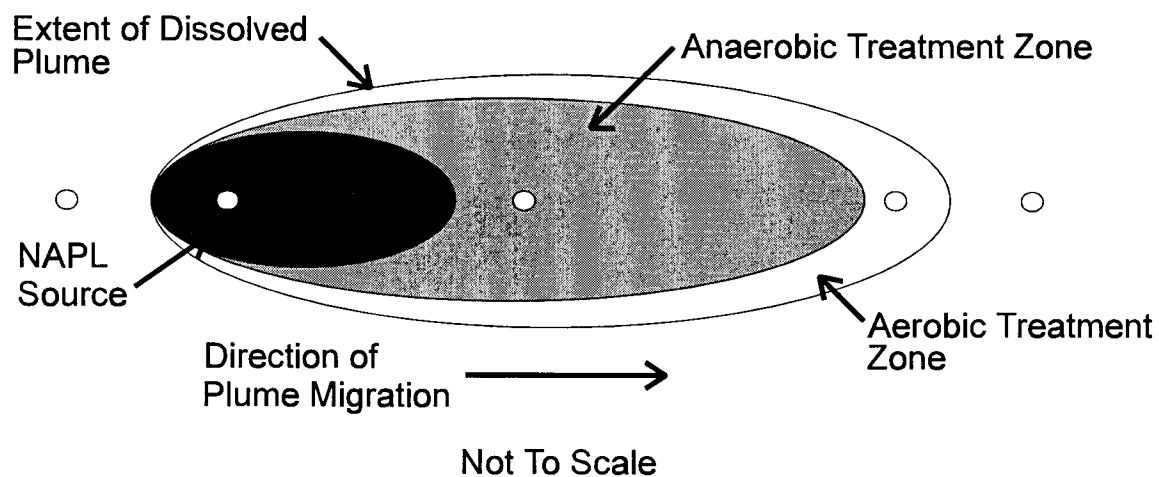
Screening for Natural Attenuation of Chlorinated Solvents - Con't

- 8) Evaluate Potential Receptor Impacts

Prepare Long-Term Monitoring Plan

- ▶ Site Point-of-Compliance Wells
- ▶ Site Long-Term Monitoring Wells
- ▶ Specify Sampling Frequency and Analytical Protocol

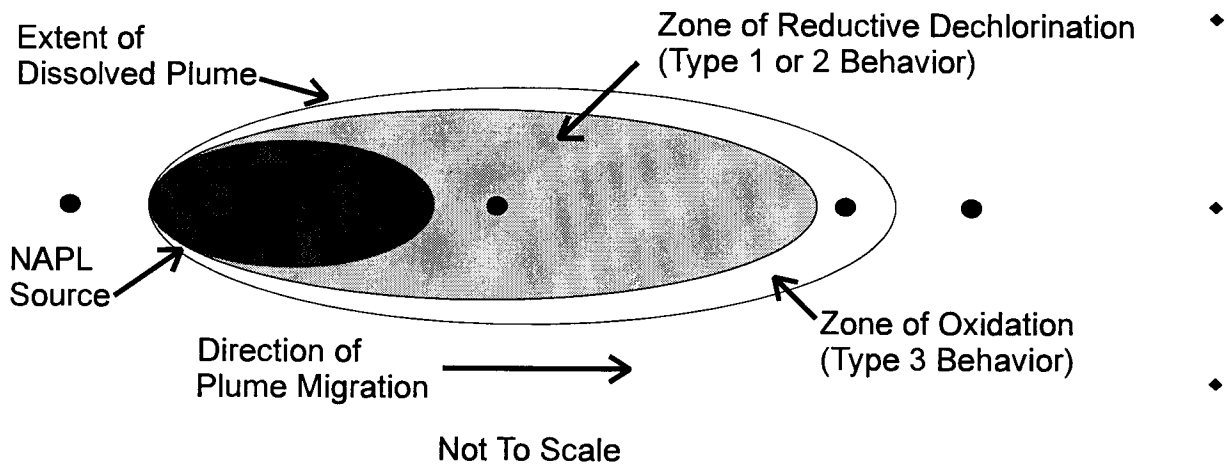
Hypothetical Long-Term Monitoring Strategy



LEGEND

- ◆ Point-of-Action Monitoring Well
- Long-Term Monitoring Well

Hypothetical Long-Term Monitoring Strategy



LEGEND

- ◆ Point-of-Action Monitoring Well
- Long-Term Monitoring Well

Contingency Plan

- ▶ Must Have a Contingency Plan Should Natural Attenuation Fail

Exit Strategy

- ▶ Must Have a Plan to End Monitoring

Conclusions

- ▶ Natural Attenuation Can Be Scientifically Supported
- ▶ Collecting Adequate and Appropriate Data is the Single-Most Important Component of the Intrinsic Remediation Demonstration
- ▶ Be Conservative and Realistic

Summary of Results

- ▶ Fuel Hydrocarbons
Intrinsic Bioremediation Protective at
>80% of Sites
- ▶ Chlorinated Solvents
Intrinsic Bioremediaion Protective at
< 20% of Sites

Why the Difference?

The Biodegradation of Fuel Hydrocarbons
is Fundamentally Different than the
Biodegradation of Chlorinated Solvents

Conclusions

- ▶ Regulatory Environment Changing
- ▶ Still Difficult to Obtain Closure of
Sites Using Natural Attenuation
for Chlorinated Solvents
- ▶ This Should Change as Our
Understanding of Natural
Attenuation Processes Matures

Conclusions

- ▶ It Is Clear That We Are Going to Have to Engineer Remediation at Many Sites Contaminated With Chlorinated Solvents
- ▶ Low Cost Carbon Addition May Hold Promise
- ▶ The Key is What Compounds to Add and the Delivery System

Conclusions

- ▶ When Tied to Low-Cost, Risk-Based Remediation, Natural Attenuation Offers the Most "Bang for the Buck"
- ▶ Typical Costs (Large Fuel-Contaminated Site)
 - ▶ Pump & Treat with Source Removal
\$2 Million +
 - ▶ Natural Attenuation with Low-Cost Source Reduction
\$200K